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(21) International Application Number: PCT/DK99/00156 (22) International Filing Date: 23 March 1999 (23.03.99) (30) Priority Data: 0404/98 23 March 1998 (23.03.98) DK (71) Applicant (for all designated States except US): NKT RESEARCH CENTER A/S [DK/DK]; Priorparken 878, DK-2605 Brøndby (DK). (72) Inventors; and (75) Inventors/Applicants (for US only): WINTHER-JENSEN, Bjørn [DK/DK]; Hornemannsgade 17, DK-2100 Copenhagen Ø (DK). ARMAND, Chaabane [DK/DK]; Fuglebakkevej 83, Stuen, DK-2000 Frederiksberg (DK). (74) Agent: HOFMAN-BANG & BOUTARD, LEHMANN & REE A/S; Hans Bekkevolds Allé 7, DK-2900 Hellerup (DK).		(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report.
(54) Title: A METHOD OF PREPARING A POLYMER COMPOSITION (57) Abstract The present invention relates to a method of preparing a highly filled polymer composition such as a flame retardant or reinforced polymer composition wherein the polymer and the filler are chemically bonded to each other. The method comprises the step of i) mixing together filler, mono- or di-carboxylic acid or anhydride thereof, radical generator and thermoplastic polymer, under conditions where said at least one radical generator is not activated; ii) activating the radical generator to form a chemically bonding between di-carboxylic acid or anhydride thereof and polymer. The method is simple and economical acceptable, and results in a highly filled polymer composition which have good mechanical strength.		

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A method of preparing a polymer composition

The present invention relates to a method of preparing a highly filled polymer composition such as a flame retardant or reinforced polymer composition.

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In recent years there has been an increasing interest in polymer compositions containing a high proportion of inorganic fillers. Such inorganic fillers are frequently used to reduce cost, improve stiffness and tensile properties, or enhance the flame retardant properties of the polymers. The presence of a high level of inorganic fillers reduces the cohesiveness and thereby the mechanical properties of the polymer composition. Further the presence of high levels of fillers may reduce the processibility of the composition, and this is undesirable, particularly if the composition is to be used in an injection moulding or extrusion process. There are different methods of improving the processibility, e.g. by using higher processing temperatures or by using processing aids. However, higher processing temperatures can cause problems with compositions containing flame retardant additives or free radical generators such as peroxides, and higher levels of processing aid adversely affect the mechanical properties of the composition, for example the mechanical strength, elongation, flexibility, low temperature performance, the flexural and impact properties. Furthermore, the processing aid is generally more flammable than the inorganic solid and hence higher levels of the processing aid are particularly undesirable in compositions intended to possess fire retardant characteristics. Another method of improving processibility is to incorporate a coupling agent into the polymer compositions.

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EP-A2-0 467 549 relates to such a polymer composition. This polymer composition is prepared by blending together

a particulate inorganic filler, a dicarboxylic acid or an anhydride and a polymer. When the filler is a hydrated alumina as it is preferred in the EP application, the dicarboxylic acid or the anhydride is bonded to the filler by an ester bonding. This known polymer composition is very much improved with respect to processibility, however. The mechanical properties still need to be improved when the polymer comprises high proportions of filler.

10

US patent No. 3,694,403 describes a polyolefin composition prepared from a polyolefin, a particulate magnesium carbonate, a dicarboxylic acid or an anhydride and a conventional radical generator such as a peroxide. When preparing the polymer composition the polyolefin, magnesium carbonate and dicarboxylic acid or anhydride is mixed together in a melt at a temperature above the softening temperature of the polyolefin. When a uniform mixture is obtained, the radical generator may be incorporated. This known polymer composition obtained is transparent and has acceptable mechanical properties, which, however, still need to be improved when the polymer composition comprises high proportions of filler.

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25 In the article "Polymeric Coupling Agents as Property Enhancers in Highly Filled Polymer Systems", Polymers & Polymer compositions, Vol. 5, No. 2, 1997, K. Hausmann and V. Flaris, a polymer composition composed of a polyolefinic polymer, a polymeric coupling agent and a filler is described. The polymeric coupling agent consists essentially of two parts: a polyolefinic backbone, chosen from polyethylene (PE), polypropylene (PP), or ethylene-vinyl acetate copolymer (EVA) which is miscible with the polyolefinic polymer, and a reactive functional group, maleic anhydride, which is previously grafted onto the polymer and which readily interacts with

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functional groups on the filler and the polymer. In this polymer composition the filler is bonded to the polymer component, and thereby the mechanical properties are highly improved. Similar polymer compositions are known from EP 0 370 517 and US 4,839,412. However all these known polymer compositions, are prepared by mixing a filler with a polymer which has been grafted with an unsaturated carboxylic acid or an unsaturated anhydride.

10 However such carboxylic acid or anhydride grafted polymer grades are very expensive, and the number of different carboxylic acid or anhydride grafted polymer grades on the market are very limited.

15 The object of the present invention is therefore to provide a new method of preparing a highly filled polymer composition which have good mechanical strength and which can be produced using a simple and economical acceptable method.

20 A further object of the invention is to provide a new method of preparing a highly filled polymer composition wherein the polymer and the filler are bonded to each other.

25 Another object of the invention is to provide a new method of preparing a highly filled polymer composition wherein the polymer and the filler are bonded to each other and which method does not require the use of a pregrafted polymer.

30

Yet another object of the invention is to provide a new simple method of preparing a highly filled polymer composition wherein the polymer and the filler are chemically bonded to each other.

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Still another object of the invention is to provide a method of preparing a highly filled polymer composition wherein the polymer and the filler are bonded to each other, and which method comprises one single mixing step.

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These and other objects are met with a method of preparing a polymer composition as defined in the claim 1. This method comprises the step of

10 i) mixing together at least one filler, at least one mono- or di-carboxylic acid or anhydride thereof, at least one radical generator and at least one polymer, under conditions where said at least one radical generator is not activated

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ii) activating said at least one radical generator for a period sufficiently long to form a chemical bonding between said at least one di-carboxylic acid or anhydride thereof and said at least one polymer.

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The filler used in the composition may be any inorganic mineral or reinforcing material, preferably in the form of sphere, flake, powder or fibre. A wide range of particulate inorganic solids may be used as fillers depending on the intended use of the polymer composition and, if desired, a mixture of particulate inorganic solids may be used as a filler. The filler or fillers may preferably be selected from the group comprising aluminium hydroxide, magnesium hydroxide, potassium hydroxide, zirconium hydroxide, calcium hydroxide, potassium titanate, antimony trioxide, barium metaborate, zinc metaborate, kaolinite, montmorillonite, talc, clay, mica, red phosphorus, barium borate, silica, white carbon, diatomaceous earth, barium sulphate, cellite, alumina, titanium oxide, zinc oxide, molybdenum disulphide, calcium phosphate, ammonium phosphate,

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ammonium bromide, ammonium borate, ammonium sulfamate, asbestos and lithopone.

5 The filler may preferably be a reinforcing fibre material in the form of organic or inorganic fibres. Inorganic fibres are more preferred particularly in the form of glass fibres or carbon fibres. The most preferred reinforcing filler material is glass fibres.

10 Another type of preferred fillers are the flame retardants. The most preferred flame retardant fillers are carbonates and particularly hydroxides.

15 The filler or fillers are selected with respect to their compatibility with the polymer in the polymer composition. As a preferred composition in accordance with the present invention, the filler is one or more halogen-free compounds which provide fire retardant and/or smoke suppressant characteristics to a polymer
20 composition. In a preferred polymer composition the particulate inorganic solid is both a fire retardant component and a smoke suppressant component. The preferred fire retardant filler is a compound which liberates water under heating, for example the material
25 referred to as hydrated alumina which may also be regarded as a form of aluminium hydroxide or a compound which liberates water at a temperature of at least 260°C, for example magnesium hydroxide (alternatively referred to as hydrated magnesia).

30

The flame retardant filler may be used in an admixture with other filler materials, for example precipitated calcium carbonate. The proportion of the fire retardant
35 filler is preferably in the range from 30 up to 100% by

weight of the total amount of filler in the polymer composition.

The preferred amount of filler material in the polymer composition depends largely on the desired degree of flame retardancy, the desired strength or the desired degree of other properties affected by the filler, of the resulting polymer composition. The amount of said at least one filler may be between 10 and 350 % by weight relative to the amount of polymers, and preferably between 60 and 200 % by weight relative to the amount of polymers. If the polymer composition is to be used in the production of cables, it is preferred that the amount of fillers is between 75 and 180 % by weight relative to the amount of polymers, and preferably between 80 and 150 % by weight relative to the amount of polymers.

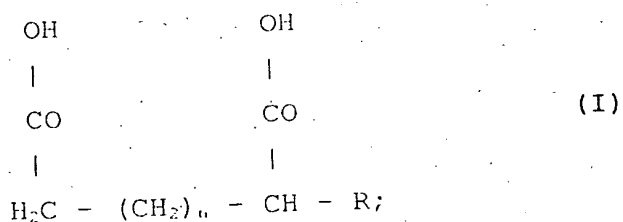
The mono- or di-carboxylic acid or anhydride thereof which may be used in the method of the invention is mono- or di-carboxylic acid or anhydride thereof or a mixture thereof having up to 100 carbon atoms preferable up to 50 carbon atoms and more preferably up to 10 carbon atoms, and having at least one double bond.

Throughout this specification the term "mono-/diacid" will be used to indicate the mono- or dicarboxylic acid or anhydride thereof and a mixture of such dicarboxylic acids or anhydrides as described above. It is very important that the mono-/diacid should comprise at least one C=C bonding (double bond). This aspect is very important because the reaction between the thermoplastic polymer and the mono-/diacid involves such bonding or more of these bondings.

The unsaturated mono-/diacid may e.g. be one of the following:

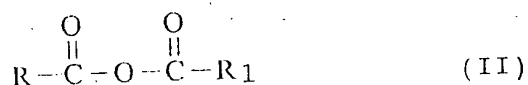
a) a mono-acid having up to 100 carbon atoms, and having at least one aliphatic substituent R,

5 b) a mono-/diacid thereof having the general formula (I)



15 c) a monocyclic diacid or anhydride thereof having at least one double bond, and having up to 100 carbon atoms, and optionally having one or more aliphatic substituent R₁ or

20 d) an anhydride having up to 100 carbon atoms, and having the general formula (II)



25 wherein R is an unsaturated aliphatic group containing up to 20 carbon atoms, preferably up to 10 carbon atoms, R₁ is a saturated or unsaturated aliphatic group containing
 30 up to 20 carbon atoms, preferably up to 10 carbon atoms, and n is either zero, one or two.

Dicarboxylic acids and anhydrides thereof are most preferred, and are in the following designated "diacids".

Preferably the mono-/diacid contains at least 4 carbon atoms. Group R and group R₁ can be a linear or branched aliphatic groups and typically are branched chain groups. The polymer composition may comprise a plurality of
5 different mono-/diacids. The polymer composition may comprise a plurality of mono-/diacids of either one or more of (a), (b), (c) and (d) which differ in the identity of the group R. The different R groups may be different isomers, for example, different branched chain
10 isomers and/or may contain different number of carbon atoms, for example, alkyl or alkenyl groups having 12 to 16 or 12 to 14 carbon atoms.

Mono-/diacids which may be used in the composition of the
15 present invention include oleic acid, palmitoleic acid, ricinoleic acid, linoleic acid, arachidonic acid, fumaric acid, itaconic acid and maleic acid and their anhydrides. Most preferred are itaconic acid and maleic acid and their anhydrides and most preferred is maleic anhydride.

20

The amount of mono-/diacid depends naturally on the type of mono-/diacid used, on the type and amount of fillers, and on the type and molecular weight of the polymers. The amount of mono-/diacid is preferably between 0.05 and 10
25 % by weight relative to the amount of polymers, and more preferably between 0.1 and 3 % by weight relative to the amount of polymers.

The radical generator may preferably be a ultrasound
30 activable, a microwave activable, a UV activable or most preferably a heat activable radical generator.

When the radical generator is a heat activable radical generator, it is preferred that the temperature in step
35 i) is below T_g, and the temperature in step ii) is above

T_a , where T_a is the activating temperature of said at least one peroxide or if more than one radical generator, the activating temperature of the radical generator having the lowest activating temperature.

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The temperature T_a is defined as the temperature at which the T_d of the radical generator is less than 1 min.

10 The heat activable radical generator is preferably a Azo compound (e.g. α, α -azobis(isobutyronitrile)) or a peroxide such as organic peroxides. The radical generator is selected with a view to the polymer in the polymer composition and the necessary activating conditions for
15 activation of the radical generator. Preferred radical generators are alkyl peroxides, peroxyesters, diacyl peroxides, hydroperoxides and/or peroxyketals. More preferred radical generators are alkyl peroxides such as dicumyl peroxide.

20 Preferred ultrasound activable radical generators are the above listed heat activable radical generators, however, the most preferred ultrasound activable radical generators are bis-(2,4-dichlorobenzoyl)peroxide and dibenzoyl peroxide.

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Preferred UV activable radical generators are the above listed heat activable radical generators, however, the most preferred UV activable radical generators are
30 dibenzoyl peroxide, tert-butyl peroxybenzoate, tert-butyl hydroperoxide and dicumyl peroxide

Preferred microwave activable radical generators are very polar peroxides, such as bis-(2,4-dichlorobenzoyl)peroxide and dibenzoyl peroxide.

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The amount of radical generator used in the method of the invention may be adjusted in relation to the amount and type of filler and thermoplastic polymer. Preferably the amount of the radical generator is between 0.001 and 2 %
5 by weight relative to the amount of polymer, and more preferably between 0.01 and 0,1 % by weight relative to the amount of polymer. The amount of radical generator for use in the initiation of the reaction between the thermoplastic polymer and the mono-/diacid, should
10 preferably be sufficiently low as to avoid any substantially crosslinking of the thermoplastic polymer under the step of reaction between the thermoplastic polymer and the mono-/diacids.

15 The thermoplastic polymer may be any type of heat processable polymer preferably comprising an olefinic component. The polymeric material is very conveniently an olefin polymer. The olefin polymer, which term is used herein to include both homopolymers and copolymers
20 containing at least 50% by weight of one, or more, olefin monomers, is a polymer of an olefin monomer which typically contains not more than ten carbon atoms, and preferably of the monomers ethylene or propylene. Thus, the olefin polymer may be any ethylene homopolymer,
25 copolymer or terpolymer, particularly high density polyethylene or linear low density polyethylene which is a copolymer of ethylene with a higher alfaolefin monomer such as butene, hexene octene or 4-methylpentene. Other ethylene polymers are the copolymers of ethylene and a
30 monomer, for example an ethylene-vinyl acetate copolymer typically one containing 10 to 40% by weight of vinyl acetate. Alternatively, the olefin polymer may be a propylene homopolymer or copolymer, for example a random copolymer of propylene with up to 8% by weight, relative
35 to the polymer, of ethylene, or a sequential polymer obtained by polymerising propylene in the essential

absence of other monomers and thereafter copolymerising a mixture of ethylene and propylene to give a polymer containing from 5 up to 30% by weight of ethylene.

- 5 Preferred polymers are homo- and copolymers of Linear low density polyethylene (LLDPE), Low density polyethylene (LDPE), High density polyethylene (HDPE), Ethylene/vinyl acetate (EVA), Ethylene-methyl-acrylate (EMA), Ethylene-acrylic-acid (EAA), Ethylene-butyl-acrylate (EBA),
10 Ethylene-ethyl-acrylate (EEA), Polypropylene (PP), Ethylene-propylene copolymer (EPM), and Ethylene-propylene-diene terpolymer (EPDM).

A particularly preferred polymer is one having a
15 molecular weight which is appropriate for a material which can be used for the production of shaped articles by an injection moulding or extrusion process. Thus, suitable olefin polymers, such as LLDPE, LDPE, HDPE, EVA, EEA, EMA, EAA, EBA and PP are those having a melt flow
20 index, measured according to ASTM Test Method 1238-79 using a 2.16 kg weight at a temperature of 230 °C, which is in the range from 0.5 g/10 minutes up to 50 g/10 minutes, preferably from 1.0 g/10 minutes up to 30 g/10 minutes.

25

The incorporation of a high proportion of fillers into the polymeric material may reduce the melt flow index, and the polymer composition containing the filler typically has a melt flow index, measured at 190 °C with
30 a weight of 2.16 kg, but otherwise under the conditions specified previously herein, of not more than 10 g/10 minutes and typically at least 0.05 g/10 minutes. In general the polymer composition preferably has a melt flow index of not more than 8 g/10 minutes.

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In the mixing step or steps it may be useful to dissolve one or more of the starting materials in an solvent which does not react with the components, but only serves to obtain a homogeneous mixture. A such solvent may e.g. be water or preferably dichloromethane.

In a first variation of the invention which is the most preferred variation, all ingredients mixed in step i) including the filler, the mono- or di-carboxylic acid or anhydride thereof, the radical generator, and the polymer is mixed together in one single mixing step, and the mixing step i) is preferably continued until a substantially homogeneous mixture is obtained.

In a second preferred variation of the invention, the mixing step i) comprises the substep

ia) mixing together the filler, the radical generator and the mono-/diacid until a homogeneous premixture is obtained, and

ib) mixing this premixture with the polymer at a temperature below T_a until a homogeneous mixture is obtained.

When mixing the premixture it is preferred that the radical generator and the mono-/diacid is dissolved in a solvent e.g. a volatile solvent, and thereafter mixed with the filler or preferably coated onto the filler.

When using the above second variation of the method according to the invention, the steps ib) and ii) may preferably be carried out simultaneously and under condition where the radical generator is activated at an temperature above T_a . When using this method, the

preparation of the polymer composition is very fast and simple.

- 5 In a further variation of this second variation the step
ia) comprises mixing together the filler and the mono-
/diacid until a homogeneous premixture is obtained, and
the step ib) comprises mixing this premixture with the
radical generator and the polymer at a temperature below
10 T_a until a homogeneous mixture is obtained.

In these above-mentioned variations, and where the
radical generator is a heat activable radical generator,
it is particularly preferred that the mixing step i) or
15 ia)/ib) respectively is carried out at a temperature
below $T_a - 30^\circ\text{C}$. Furthermore, it is preferred that said
mixture in step ii) is heated to a temperature of at
least $T_a + 30^\circ\text{C}$ for a period sufficiently to form a
chemically bonding between the mono-/diacid and the
20 polymer, preferably this period is about $5 \times T_a$ of the
heat activable radical generator or more.

In a third variation of the invention the mixing step i)
and the heating step ii) are carried out simultaneously
25 in one single step i-ii). In a subvariation of this third
variation, a step similar to step ia) as defined above
of mixing together the filler, the radical generator and
the mono-/diacid until a homogeneous premixture is
obtained is carried out before the step ib-ii) of mixing
30 this premixture with the polymer and heating.

In the third variation of the invention, and where the
radical generator is a heat activable radical generator,
it is preferred that the single step i-ii) or ib-ii) is
35 initiated at a temperature below $T_a - 30^\circ\text{C}$ and said step
i-ii) comprises heating the filler, the peroxide, the

mono-/diacid and the polymer to a temperature of at least $T_g + 30^\circ\text{C}$ for a period sufficiently long to form a chemical bonding between the mono-/diacid and the polymer, preferably this period is about $5 \times T_g$ of the heat activable radical generator or more.

In the mixing step where the polymer is mixed with other components, the temperature should preferably be sufficient to soften the polymer. This means that the temperature should be selected to be T_g of the polymer or higher. The mixing time depends largely on the equipment used. However, 10 minutes are usually sufficient.

The chemical bondings between the mono-/diacid and the polymer are preferably covalent bondings, and these will usually be established within about 10 seconds - 10 minutes. In most situations, a reaction temperature of about 160°C should be sufficient.

A particular preferred second method of preparing a polymer composition is claimed in claim 25 and comprises the step of

a) mixing together at least one filler, at least one mono- or di-carboxylic acid or anhydride thereof, at least one heat activable radical generator and under conditions where said at least one heat activable radical generator is not activated until a homogeneous premixture is obtained, and

b) mixing said homogeneous premixture with at least one polymer under conditions where said at least one heat activable radical generator is activated and keeping said conditions for a period sufficiently long to form a chemical bonding between said at least one di-carboxylic acid or anhydride thereof and said at least one polymer.

In this second method, the preferred mono-/diacid, the preferred filler, the preferred heat activable radical generator and the preferred polymer is as described above. further the premixture preferably is in the form of coated filler as described above.

In the above described third variation and second method of the invention, the polymer composition is preferably made in a continuous process e.g. in a compounding extruder. The temperature in the compounding extruder varies from about T_g of the initial thermoplastic polymer to above T_i of the radical generator. The starting materials are feed into the extruder in the low-temperature end and passes through the extruder.

The polymeric compositions in accordance with the present invention may be formed into shaped articles by any suitable technique, particularly by injection moulding or extrusion.

The polymer compositions may be obtained using any suitable blending technique, particularly a melt mixing technique using, for example, a two roll mill or, preferably, an internal mixer such as a Banbury or Brabender mixer. The mixing may be effected using a compounding extruder which may be a single screw extruder or, preferably, a twin screw extruder.

The polymer composition may be formed directly into a shaped article but more conveniently is first formed into granules which are subsequently injection moulded or extruded to form the desired shaped article. The polymer composition can for example be used for coating electrical conductors, as fire retardant panels, as a floor covering or for preparing cables.

In the following various aspects of the present invention are described.

5 In the examples 1-12, the following materials were used:

Evatane 2083 (EVA) delivered from elf Atochem.

Maleic anhydride delivered from Aldrich.

10 ATH Apyral 60 (alumina trihydrate) delivered from WAW
aluminium AG.

Dicumyl peroxide delivered from Ciba.

Dichloro methane delivered from Aldrich.

15 The mixer used, was a HAAKE record 9000.

Example 1

The mixer was started and the temperature was set at 90 °C. The speed was set at 20 rotations per minute (r/min).
20 152 g Evetane, 3.1 g maleic anhydride, 216 g ATH and 0.062 g of peroxide were added simultaneously to the mixer. After 10 minutes the temperature was adjusted to 170 °C and the speed was raised to 50 r/min. After 10 minutes the mixing was terminated and the polymer melt
25 was removed from the mixer and granulated (using a granulator: Meltic). The granulate was extruded to a thickness of about 1,5 mm and cut into "Dump-bell" test pieces (CEI-IEC 1 166/93).

30 The test pieces of the resulting polymer composition were tested (using an Instron 4301) with respect to elongation at rupture and tensile strength, and the results are listed in table 1.

Sample No.	1	2	3	4	5	6
EVA (Parts by weight)	100 (152 g)	100	100	100	100	100
Maleic anhydride (Parts by weight)	2 (3.1 g)	0.3	1	1.5	0	3
Dicumyl peroxide (ppm EVA)	400 (0.062 g)	60	200	300	0	600
ArH (Parts by weight)	140 (216 g)	140	140	140	140	140
Elongation at rupture (%)	247	154	245	252	148	217
Tensile strength (Mpa)	14,7	4,89	8,6	11,9	5,1	16,3

Table 1.

Examples 2-10

5

These polymer compositions were prepared and tested as the polymer composition in example 1. The amount of starting materials is listed in table 1, as well as the test results.

10

It should be observed that the examples 5, 7 and 10 are not according to the invention, because no maleic anhydride/ peroxide was added.

15

Example 11

ATH was coated with maleic anhydride and peroxide: 10 g maleic anhydride and 0.2 g peroxide was dissolved in 300 ml dichloromethane. 1 kg ATH was added to a high speedmixer at a speed of 1000 r/min. After 5 minutes the dichloromethane solution was injected into the mixer. The mixing was carried out for about 15 minutes in order to evaporate the dichloromethane.

25

About 213 g of the coated ATH and 152 g Evatane were added simultaneously to the HAKKE mixer and the preparation of the polymer composition was continued as described above for example 1, and the resulting polymer compositions were tested as the polymer composition of example 1. The test results are listed in table 2.

30

Examples 12

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This polymer composition was prepared and tested as the polymer composition in example 11. The amount of starting

materials is listed in table 2, together with the test results.

Sample No.	11	12
EVA (Parts by weight)	100 (152 g)	100
ATH Coated with (1 W% of ATH) maleic anhydride and (200ppm of ATH) dicumyl peroxide	140 (213 g)	
ATH Coated with (1 W% of ATH) maleic acid and (200ppm of ATH) dicumyl peroxide		140
Elongation at rupture (%)	261	246
Tensile strength (Mpa)	11.6	11.9

5

Table 2.

Examples 13-14

- 10 In example 13 (according to the invention) and example 14 (a comparative example), the following starting materials were used:

- 15 LLDPE polymer: Clearflex 508 cl, delivered from Polymeri.
Glass fibres: length about 4 cm, thickness about 10 μ m.
Maleic anhydride delivered from Aldrich.
Dicumyl peroxide delivered from Ciba.

- 20 The amounts used of the starting materials are listed in table 3.

The mixer used, was a HAAKE record 9000.

The mixer was started and the temperature was set at 135°C. The speed was set at 50 rotations per minute (r/min). LLDPE, glass fibres, maleic anhydride and dicumyl were added simultaneously to the mixer. After 10 minutes the temperature was adjusted from 135 °C to 185°C over a period of about 5 minutes. After 10 minutes the mixing was terminated and the polymer melt was removed from the mixer and formed into "Dump-bell" test pieces and tested as in example 1. The test results are listed in table 3.

	13	14
LLDPE (W%)	59	60
Glass fibres (W%)	40	40
Maleic anhydride (W%)	1	
Dicumyl peroxide (ppm of compound)	400	
Elongation at rupture (%)	2,7	16,8
Tensile strength (Mpa)	23,35	10,56

Table 3.

Claims:

1. A method of preparing a polymer composition comprising at least 10 % by weight of filler, wherein the polymer and the filler are chemically bonded to each other, which method comprises the step of

i) mixing together at least one filler, at least one mono- or di-carboxylic acid or anhydride thereof, at least one radical generator and at least one polymer, under conditions where said at least one radical generator is not activated

ii) activating said at least one radical generator for a period sufficiently long to form a chemical bonding between said at least one di-carboxylic acid or anhydride thereof and said at least one polymer,

said at least one filler being an inorganic mineral or reinforcing material,

said at least one mono- or di-carboxylic acid or anhydride thereof having up to 100 carbon atoms, and having at least one double bond,

said at least one polymer being a thermoplastic polymer.

2. A method of preparing a polymer composition as claimed in claim 1, wherein said at least one radical generator is activated by microwave.

3. A method of preparing a polymer composition as claimed in claim 1, wherein said at least one radical generator is activated by ultrasound.

4. A method of preparing a polymer composition as claimed in claim 1, wherein said at least one radical generator is activated by heat.

5 5. A method of preparing a polymer composition as claimed in claim 4, wherein the temperature in step i) is below T_a , and the temperature in step ii) is above T_a , where T_a is the activating temperature of said at least one radical generator or if more than one radical generator,
10 the activating temperature of the radical generator having the lowest activating temperature.

6. A method of preparing a polymer composition as claimed in any of the claims 1-5, wherein step i) is continued
15 until a homogeneous mixture is obtained.

7. A method of preparing a polymer composition as claimed in any of the claims 1-6, wherein step i) comprises the substeps
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ia) mixing together said at least one filler, said at least one radical generator, and said at least one mono- or di-carboxylic acid or anhydride thereof until a homogeneous premixture is obtained, and
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ib) mixing said homogeneous premixture with said at least one polymer under conditions where said at least one radical generator is not activated, until a homogeneous mixture is obtained.
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8. A method of preparing a polymer composition as claimed in claim 7, wherein the premixture is obtained by dissolving said at least one radical generator, and said at least one mono- or di-carboxylic acid or anhydride thereof in a solvent, coating said at least one filler
35 with the solution, and evaporating said solvent.

9. A method of preparing a polymer composition as claimed in claims 7 and 8, wherein said at least one radical generator is a heat activated radical generator, and
5 wherein step ia) and/or ib) of mixing together premixture and polymer is carried out at a temperature below $T_g - 30$ °C.

10. A method of preparing a polymer composition as
10 claimed in claim 5, wherein said step i) of mixing together filler, mono- or di-carboxylic acid or anhydride thereof, peroxide and polymer is carried out at a temperature below $T_g - 30$ °C.

15 11. A method of preparing a polymer composition as claimed in any of the claims 9 or 10, wherein said mixture in step ii) is heated to a temperature of at least $T_g + 30$ °C for a period sufficiently long to form a chemical bonding between said at least one mono- or di-
20 carboxylic acid or anhydride thereof and said at least one polymer.

12. A method of preparing a polymer composition as claimed in claim 1, wherein said step i) and said step
25 ii) are carried out simultaneously in one single step i-ii), and said single step i-ii) is initiated under conditions where at least one radical generator is not activated, followed by an activating of said at least one radical generator for a period sufficiently long to form
30 a chemical bonding between said at least one mono- or di-carboxylic acid or anhydride thereof and said at least one polymer.

13. A method of preparing a polymer composition as
35 claimed in claim 12, wherein said at least one radical generator is a heat activated radical generator, and

wherein said single step i-ii) is initiated at a temperature below $T_g - 30$ °C, and said step i-ii) comprises heating said at least one filler, said at least one radical generator, said at least one mono- or di-carboxylic acid or anhydride thereof, and said at least one polymer to a temperature of at least $T_g + 30$ °C for a period sufficiently long to form a chemical bonding between said at least one mono- or di-carboxylic acid or anhydride thereof and said at least one polymer.

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14. A method of preparing a polymer composition as claimed in any of the claims 1-13, wherein said at least one thermoplastic polymer comprises an olefinic component preferably said at least one polymer is an olefin polymer containing at least 50 % by weight of the monomers ethylene or propylene and more preferably said at least one polymer is selected between homo- and copolymers of linear low density polyethylene (LLDPE), low density polyethylene (LDPE), high density polyethylene (HDPE), ethylene/vinyl acetate (EVA), Ethylene-methyl-acrylate (EMA), Ethylene-acrylic-acid(EAA), Ethylene-butyl-acrylate (EBA), Ethylene-ethyl-acrylate (EEA), polypropylene (PP).

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15. A method of preparing a polymer composition as claimed in any of the claims 1-14, wherein said at least one diacid or anhydride is itaconic acid or maleic acid or their anhydrides, more preferably maleic anhydride.

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16. A method of preparing a polymer composition as claimed in any of the claims 1-15, wherein said at least one filler being an inorganic mineral selected from carbonates and hydroxides, preferably selected from alumina trihydrates, magnesium hydroxide.

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17. A method of preparing a polymer composition as claimed in any of the claims 1-15, wherein said at least one filler being a reinforcing material selected from organic and inorganic fibres, preferably selected from glass fibres and carbon fibres.

18. A method of preparing a polymer composition as claimed in any of the claims 1 and 3-17, wherein said at least one radical generator is a peroxide, preferably being selected from alkyl peroxides, peroxyesters, diacyl peroxides, hydroperoxides and peroxyketals, more preferably in the form of dicumyl peroxide.

19. A method of preparing a polymer composition as claimed in any of the claims 1-17, wherein said at least one radical generator is microwave activable and is selected between tert-butyl hydroperoxide and tert-butyl perbenzoate.

20. A method of preparing a polymer composition as claimed in any of the claims 1-17, wherein said at least one radical generator is ultrasound activable and is selected between bis-(2,4-dichlorobenzoyl)peroxide and dibenzoyl peroxide.

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21. A method of preparing a polymer composition as claimed in any of the claims 1-20, wherein the amount of said at least one filler is between 10 and 350 % by weight relative to the amount of polymer, and preferably between 60 and 200 % by weight relative to the amount of polymer.

22. A method of preparing a polymer composition as claimed in any of the claims 1-21, wherein the amount of said at least one mono- or di-carboxylic acid or

anhydride thereof is between 0.05 and 10 % by weight relative to the amount of polymer, and preferably between 0.1 and 3 % by weight relative to the amount of polymer.

5 23. A method of preparing a polymer composition as claimed in any of the claims 1-22, wherein the amount of said at least one radical generator is between 0.001 and 2 % by weight relative to the amount of polymer, and preferably between 0.01 and 0,1 % by weight relative to
10 the amount of polymer.

24. A method of preparing a polymer composition as claimed in any of the claims 1-23, wherein said mixing (step i)) and said heating (step ii)) are carried out in
15 a continuously compounding process.

25. A method of preparing a polymer composition comprising at least 10 % by weight of filler, wherein the polymer and the filler are chemically bonded to each
20 other, which method comprises the step of

a) mixing together at least one filler, at least one mono- or di-carboxylic acid or anhydride thereof, at least one heat activable radical generator and under
25 conditions where said at least one heat activable radical generator is not activated until a homogeneous premixture is obtained, and

b) mixing said homogeneous premixture with at least one
30 polymer under conditions where said at least one heat activable radical generator is activated and keeping said conditions for a period sufficiently long to form a chemically bonding between said at least one di-carboxylic acid or anhydride thereof and said at least
35 one polymer,

said at least one filler being an inorganic mineral or reinforcing material,

5 said at least one mono- or di-carboxylic acid or anhydride thereof having up to 100 carbon atoms, and having at least one double bond,

said at least one polymer being a thermoplastic polymer.

10 26. A method of preparing a polymer composition as claimed in claim 25, wherein said at least one radical generator is activated by microwave.

15 27. A method of preparing a polymer composition as claimed in claim 25, wherein said at least one radical generator is activated by ultrasound.

20 28. A method of preparing a polymer composition as claimed in claim 25, wherein said at least one radical generator is activated by heat.

25 29. A method of preparing a polymer composition as claimed in any of the claims 26-28, wherein the premixture is obtained by dissolving said at least one radical generator, and said at least one mono- or di-carboxylic acid or anhydride thereof in a solvent, coating said at least one filler with the solution, and evaporating said solvent.

30 30. A method of preparing a polymer composition as claimed in claims 29, wherein said at least one radical generator is a heat activated radical generator, and wherein step a) of mixing together premixture and polymer is carried out at a temperature below $T_g - 30$ °C.

31. A method of preparing a polymer composition as claimed in any of the claims 29 or 30, wherein said mixture in step b) is heated to a temperature of at least $T_a + 30\text{ }^{\circ}\text{C}$ for a period sufficiently long to form a chemical bonding between said at least one mono- or di-carboxylic acid or anhydride thereof and said at least one polymer.

32. A method of preparing a polymer composition as claimed in any of the claims 25-31, wherein said at least one thermoplastic polymer comprises an olefinic component preferably said at least one polymer is an olefin polymer containing at least 50 % by weight of the monomers ethylene or propylene and more preferably said at least one polymer is selected between homo- and copolymers of linear low density polyethylene (LLDPE), low density polyethylene (LDPE), high density polyethylene (HDPE), ethylene/vinyl acetate (EVA), Ethylene-methyl-acrylate (EMA), Ethylene-acrylic-acid(EAA), Ethylene-butyl-acrylate (EBA), Ethylene-ethyl-acrylate (EEA), polypropylene (PP).

33. A method of preparing a polymer composition as claimed in any of the claims 25-32, wherein said at least one diacid or anhydride is itaconic acid or maleic acid or their anhydrides, more preferably maleic anhydride.

34. A method of preparing a polymer composition as claimed in any of the claims 25-33, wherein said at least one filler being an inorganic mineral selected from carbonates and hydroxides, preferably selected from alumina trihydrates, magnesium hydroxide.

35. A method of preparing a polymer composition as claimed in any of the claims 25-34, wherein said at least one filler being a reinforcing material selected from organic and inorganic fibres, preferably selected from glass fibres and carbon fibres.

36. A method of preparing a polymer composition as claimed in any of the claims 25 and 27-35, wherein said at least one radical generator is a peroxide, preferably being selected from alkyl peroxides, peroxyesters, diacyl peroxides, hydroperoxides and peroxyketals, more preferably in the form of dicumyl peroxide.

37. A method of preparing a polymer composition as claimed in any of the claims 25-35, wherein said at least one radical generator is microwave activable and is selected between tert-butyl hydroperoxide and tert-butyl perbenzoate.

38. A method of preparing a polymer composition as claimed in any of the claims 25-35, wherein said at least one radical generator is ultrasound activable and is selected between bis-(2,4-dichlorobenzoyl)peroxide and dibenzoyl peroxide.

39. A method of preparing a polymer composition as claimed in any of the claims 25-38, wherein the amount of said at least one filler is between 10 and 350 % by weight relative to the amount of polymer, and preferably between 60 and 200 % by weight relative to the amount of polymer.

40. A method of preparing a polymer composition as claimed in any of the claims 25-39, wherein the amount of said at least one mono- or di-carboxylic acid or

anhydride thereof is between 0.05 and 10 % by weight relative to the amount of polymer, and preferably between 0.1 and 3 % by weight relative to the amount of polymer.

- 5 41. A method of preparing a polymer composition as claimed in any of the claims 25-40, wherein the amount of said at least one radical generator is between 0.001 and 2 % by weight relative to the amount of polymer, and preferably between 0.01 and 0,1 % by weight relative to
10 the amount of polymer.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 99/00156

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 23/04, C08K 5/09, C08K 3/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08K, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	File WPI, Derwent accession no. 77-06414, Idemitsu Kosan Co Ltd: "Polyolefin resin of excellent mechanical strength - prepd. from compsn. including radical generator and inorganic filler coated with liq. rubber or unsatd. carboxylic acid (deriv.)"; & JP,A,51142052, 761206 DW7704; JP,A,53020537B, 780627 DW7829	1-41

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 99/00156

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0467549 A2 (IMPERIAL CHEMICAL INDUSTRIES PLC), 22 January 1992 (22.01.92), abstract --	1-41
A	File WPI, Derwent accession no. 89-147430, Asahi Chem Ind Co Ltd: "Polyolefin resin compsn. - comprises polyolefin resin filled with active inorganic filler and polyolefin resin modified with unsatd. carboxylic acid"; & JP,A,1090235, 890406 DW8920 --	1-41
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A	File WPI, Derwent accession no. 83-40119, Sumitomo Chem Co Ltd: "Glass fibre-reinforced resin composite with high mechanical strength - in which glass fibres are treated with alumina and/or silica, or silance cpd."; & JP,A,58045262, 830316 DW8317 --	1-41
A	US 4845146 A (TAKASHI INOUE ET AL), 4 July 1989 (04.07.89), abstract -----	1-41

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Information on patent family members

01/06/99

International application No.

PCT/DK 99/00156

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